

Novel Electrolyte Development with High Lithium-Ion Transference Number (Hi-LiT) for Extreme Fast Charging

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Overview

Timeline

- Project Start: 8/15/18
- Project End: 8/14/20
- Percent Complete: 80%

Budget

- \$50k in FY18
- \$475k in FY19
- \$375k in FY20

Barriers

- Barriers addressed
 - reducing the production cost of a BEV cell to \$80/kWh, increasing the range of BEVs to 300 miles, and decreasing the charging time to 15 minutes or less.

Collaborations

- Interactions/Collaborations
 - David Robertson (Argonne National Lab)
 - Guangsheng Zhang (UA Huntsville)
 - Feng Lin, Michael Schulz (Virginia Tech)
 - Kejie Zhao (Purdue University).
 - Jue Liu (SNS, ORNL).
- Project Lead: ORNL
- Project Partner: XALT Energy

Objectives & Relevance

- **Main Objective**: To implement a novel high-Li-ion-transference (Hi-LiT) electrolyte and enable a 10-minute charge of cells with 180 Wh/kg energy density by increasing t_{Li^+} from 0.36 to 0.75 while maintaining a relatively high conductivity of 4-10 mS/cm.
- **Relevance to Barriers and Targets**
- At high charge rate, Li ion concentration gradient builds up and leads to Li ion depletion in graphite electrode.
 - Li plating, especially Li dendrite growth, leading to poor cycling performance.
 - Abruptly end of charging step, leading to low energy density.
 - Increased cell temperature, leading to electrolyte degradation and poor cycling.
- The proposed technology is to implement a novel non-aqueous electrolyte system with high Li ion transference number (Hi-LiT) for high energy density Li-ion cells. It will meet the battery performance target of delivering 180 Wh/kg of stored energy to the cell during 10-minute charging at the beginning of life and achieving less than 20% fade in specific energy after 500 cycles (144 Wh/kg).

Task Milestones and Progress

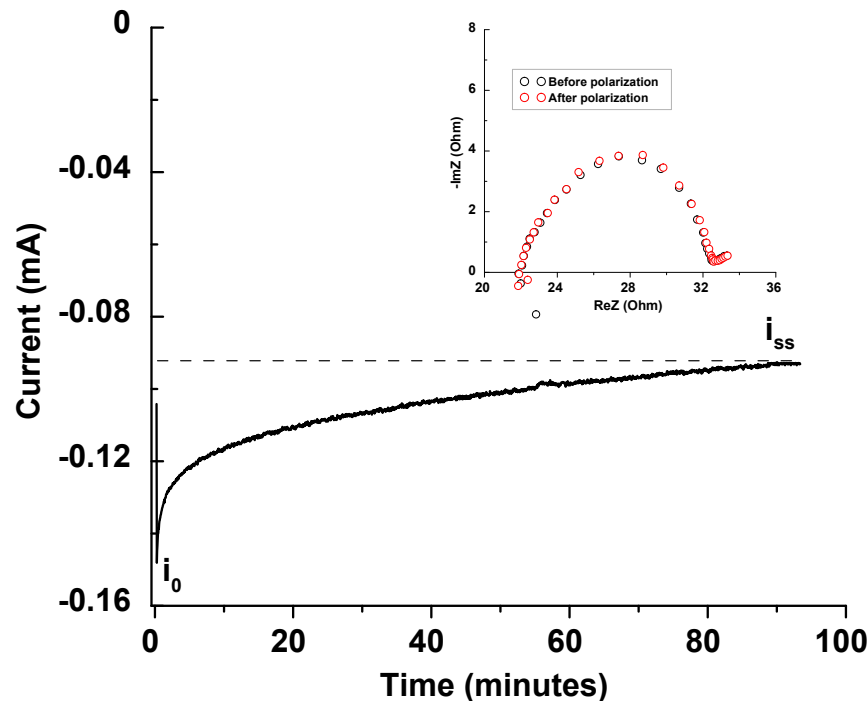
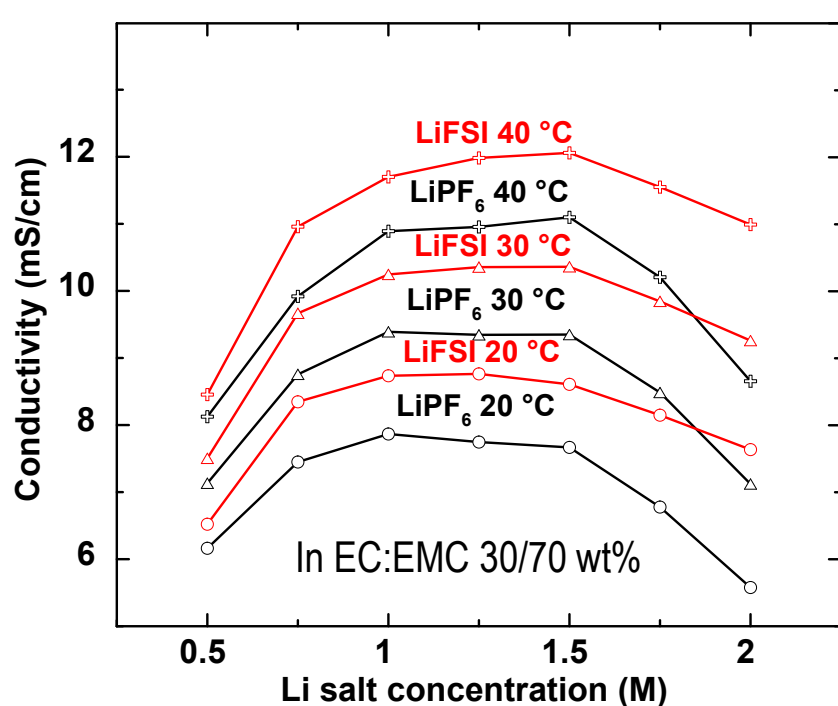
- SMART Milestone – Achieve 10 % higher capacity under 10-minute charge protocol with ORNL V1 electrolyte compared to baseline electrolyte (1.2 M LiPF_6 in ethylene carbonate/ethyl methyl carbonate EC/EMC 3/7 by weight). If No-go, the strategy of the concept will be re-evaluated and modified to meet the project goal. (8/31/2019)
 - ✓ The decision was Go based on the cell performance tested.
- Milestone 5 – Gen 1 electrolyte performance with different XFC protocols (11/30/2019).
 - ✓ Completed
- Milestone 6 – Electrolyte viscosity and conductivity modification (2/29/2020).
 - ✓ Completed
- Milestone 7 – Finalize ORNL V2 electrolyte formulation to achieve 180 Wh/kg energy density. (5/31/2020)
 - ✓ In progress

Approach

Three highly interrelated approaches are implemented:

- (1) Innovative Li salt formulation to increase Li ion transference number. We investigated the LiFSI and other novel Li salts to slow anion mobility, thereby increasing the Li ion transport portion in the total current.
- (2) Formulations with multiple solvent systems to provide better Li ion mobility and suppress Li plating. We investigated the utilization of co-solvent systems for Hi-LiT electrolyte. This approach will further enhance the Li ion transport, facilitate fast charge-transfer due to less EC complexation with Li^+ and suppress Li plating due to improved anode resistance for long term cycling performance.
- (3) Additives to further immobilize anions and dissociate cations in the electrolyte. We investigated the addition of low-MW compounds with stable electrochemical properties. The additive will further decrease the mobility of anions and increase the mobility of Li^+ by dissociating it from anions.

LiFSI shows higher conductivity and higher $t(\text{Li}^+)$ compared to LiPF_6



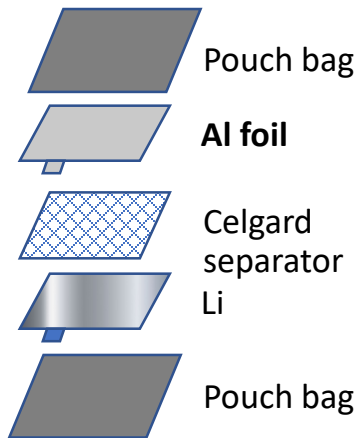
- LiFSI shows 10% improvement in conductivity compared to LiPF_6 , especially at high molarity.
- $t(\text{Li}^+)$ is ~ 0.50 , compared to 0.30 in LiPF_6 .

LiFSI based electrolyte corrosion test: no corrosion on Al foil with additives

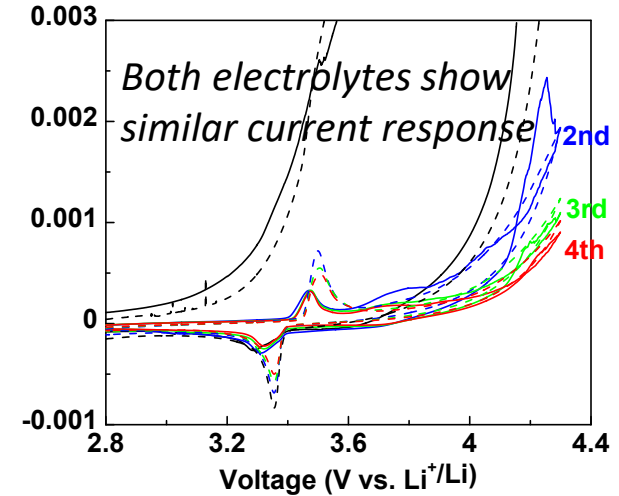
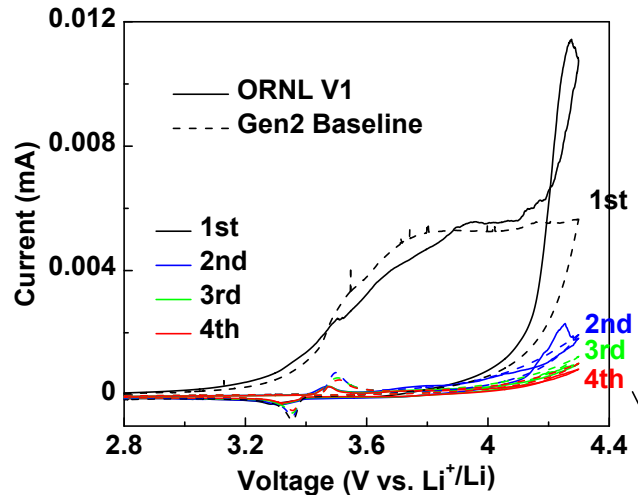
Gen2 baseline: 1.2 M LiPF_6 in EC:EMC 30:70 wt%

ORNL electrolyte: 1.5 M LiFSI in EC:EMC:DMC with **additives**

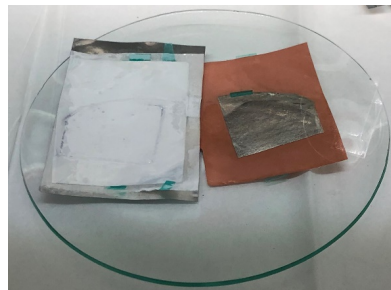
Cyclic voltammetry: 0.1 mV/s between 2.6-4.3 V (vs. Li^+/Li)



Note: same plot, but Y axis in right figure to show 2nd, 3rd and 4th cycle



After CV scanning, cells were opened in glove box



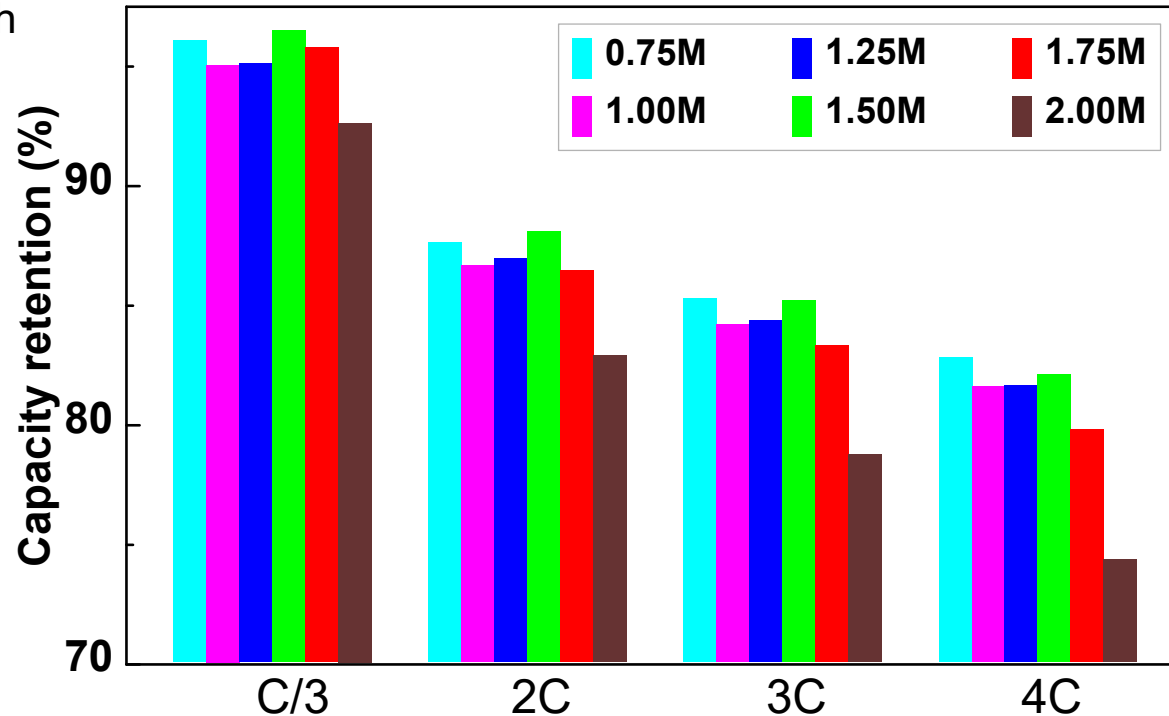
No sign of corrosion for either ORNL V1 or Gen2 baseline



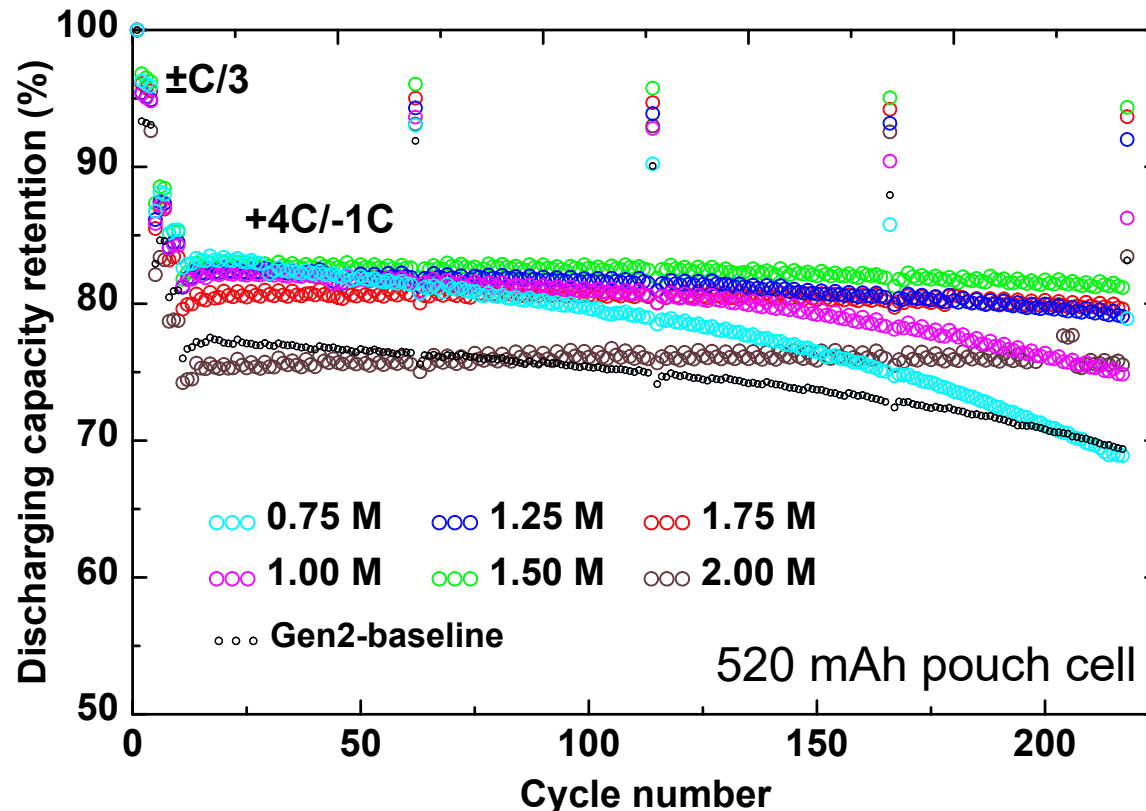
- ❑ With proper additive in electrolyte formulation, LiFSI shows similar current response in CV test.
- ❑ No Al corrosion was observed in ORNL V1 electrolyte.

Rate performance of different molarities using LiFSI salt shows different capacity retention behavior

- **Electrolyte** compositions: LiFSI in EC:EMC:DMC 40:30:30 wt% (with additive A)
- **Electrodes:**
 - NMC622 @ 3 mAh/cm²
 - graphite @ 3.3 mAh/cm²
- **Li-ion Cells:** 500 mAh pouch cell
- Good fast charging capacity retained from 0.75-1.50 M electrolyte.
- Fast charging capacity starts to decrease for 1.75 M and 2.00 M.



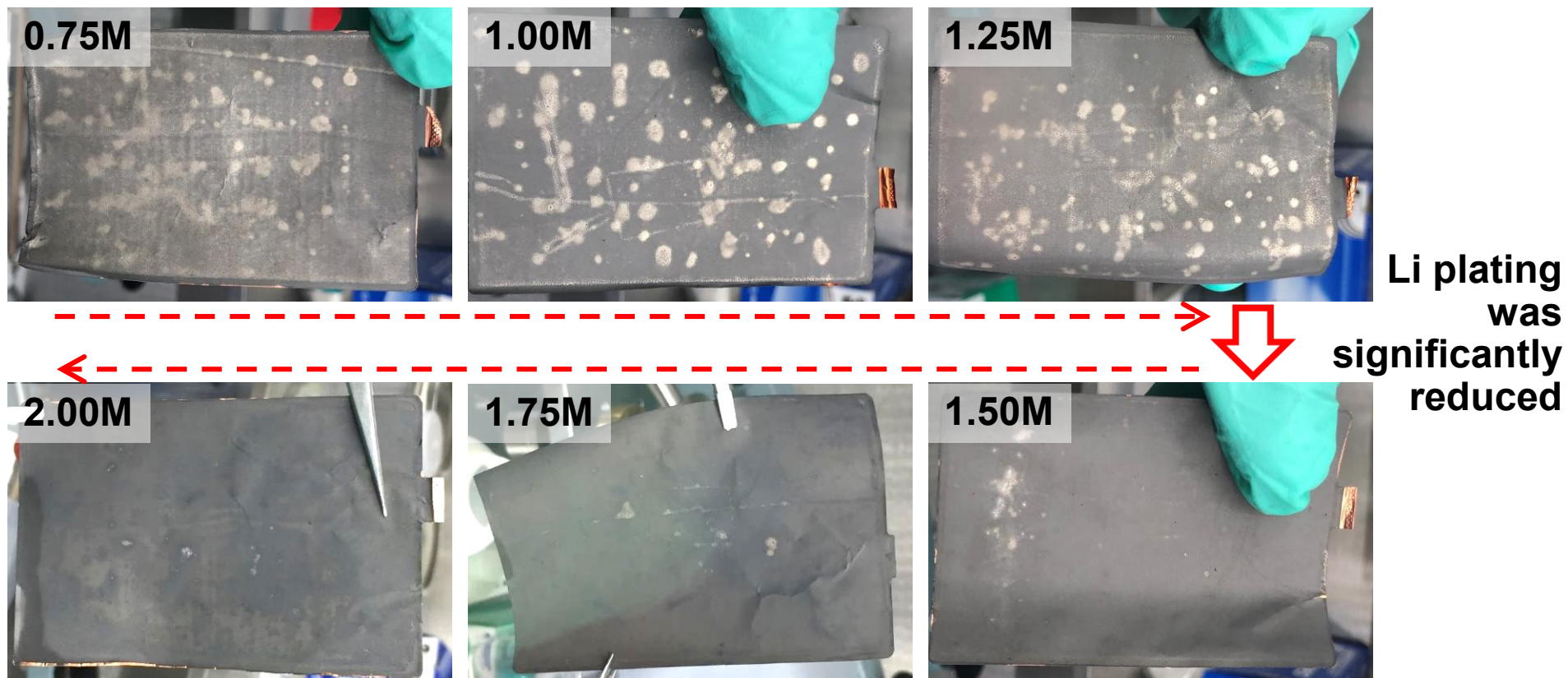
Long term cycling of different molarities shows 1.5 M yielded best performance



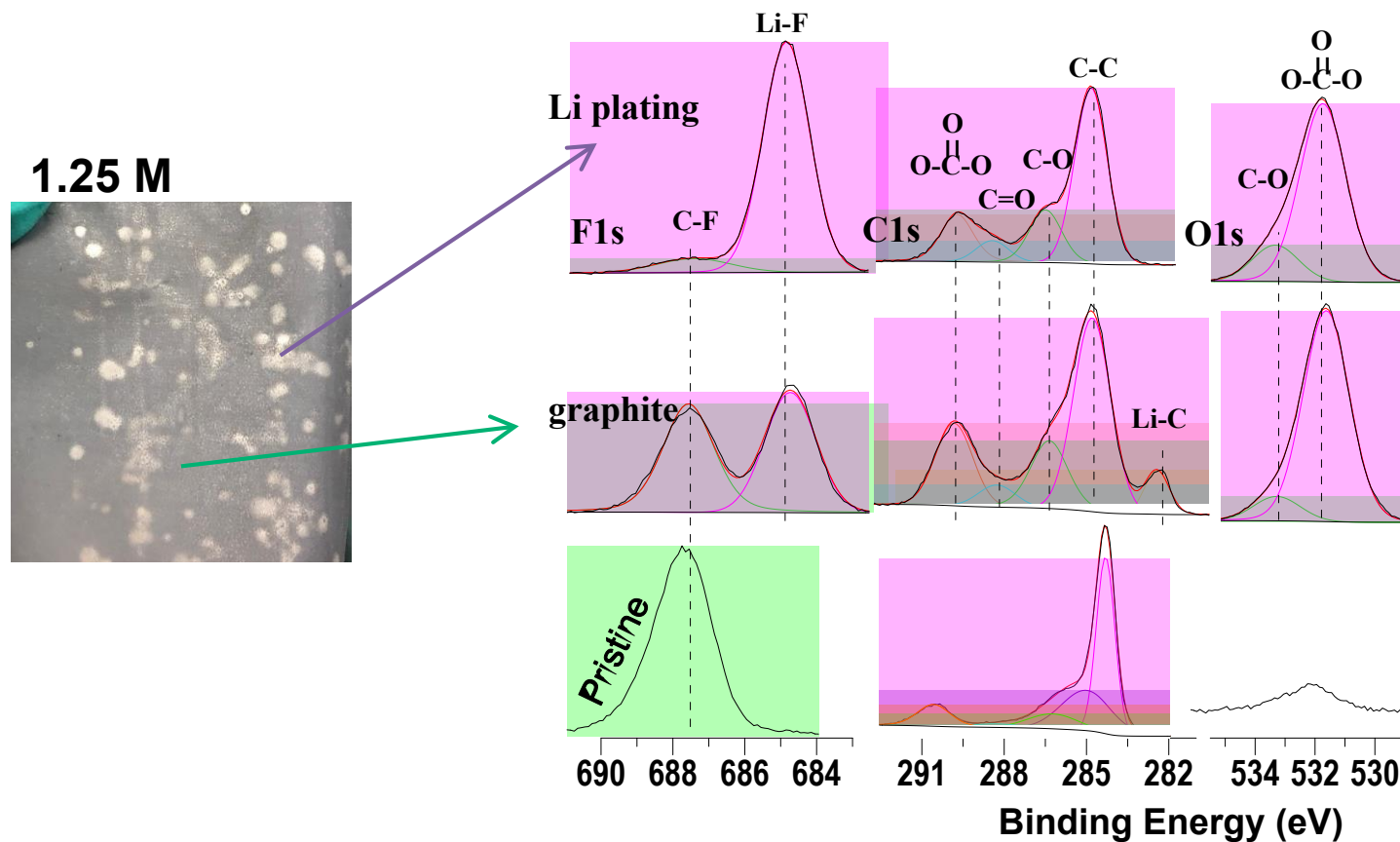
Long term cycling performance for fast charging is strongly correlated with the electrolyte molarity.

The performance is improved with the increase of molarity.

Graphite electrodes after 200 cycles show a strong correlation between electrolyte molarity and Li plating



Different electrode/electrolyte interphases for plated Li and graphite areas

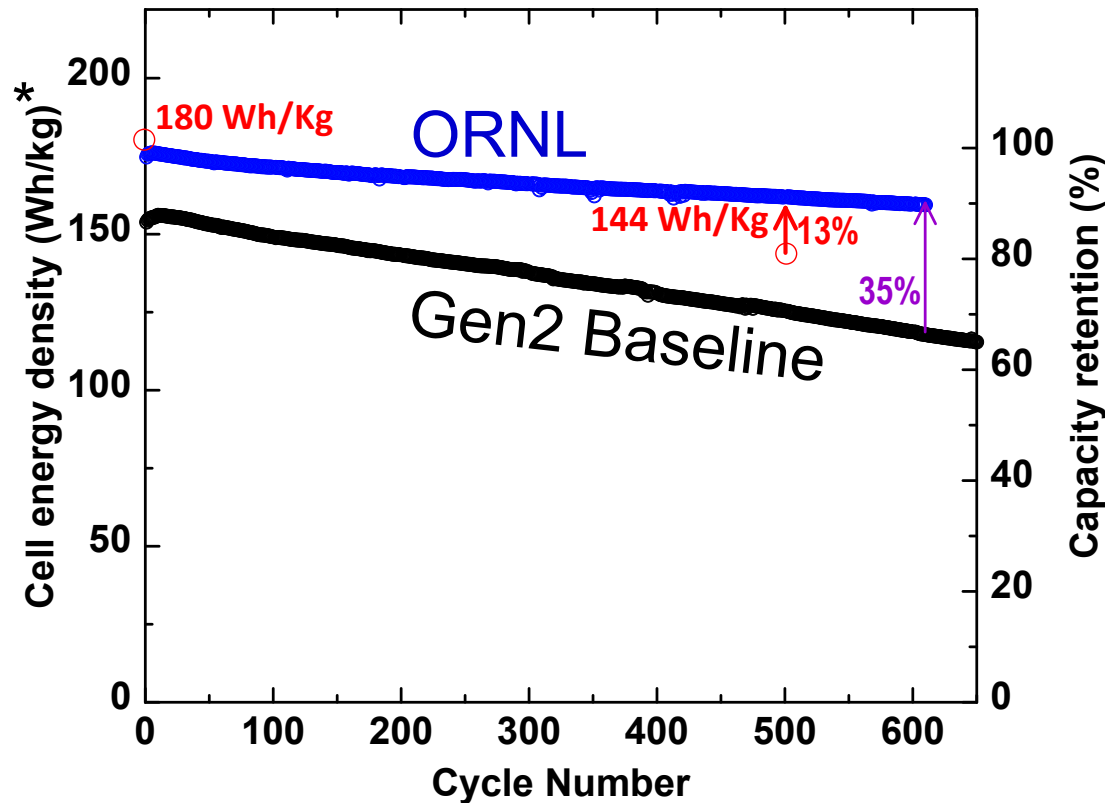


For the F1s spectra, C-F is from the PVDF binder in the electrode. In the graphite area, we can still see a pretty good signal of binder, but very minimal in Li plating area.

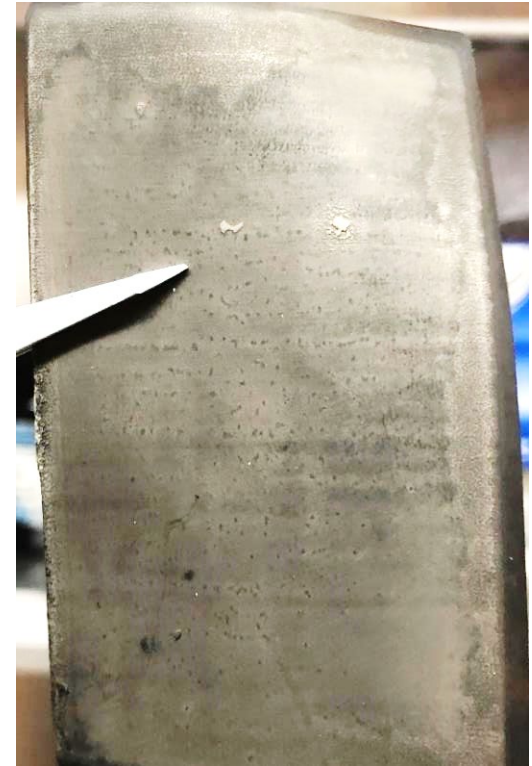
For the C1s and O1s, they are similar, both have some organic ether or carbonate species. Except for C1s in graphite area, we can still detect some Li-C bond from Li_xC intercalation compounds.

Pouch cells using ORNL V1 electrolyte show **13% higher energy density than goal** and **35% improvement over baseline**

ORNL extreme fast charging cycling

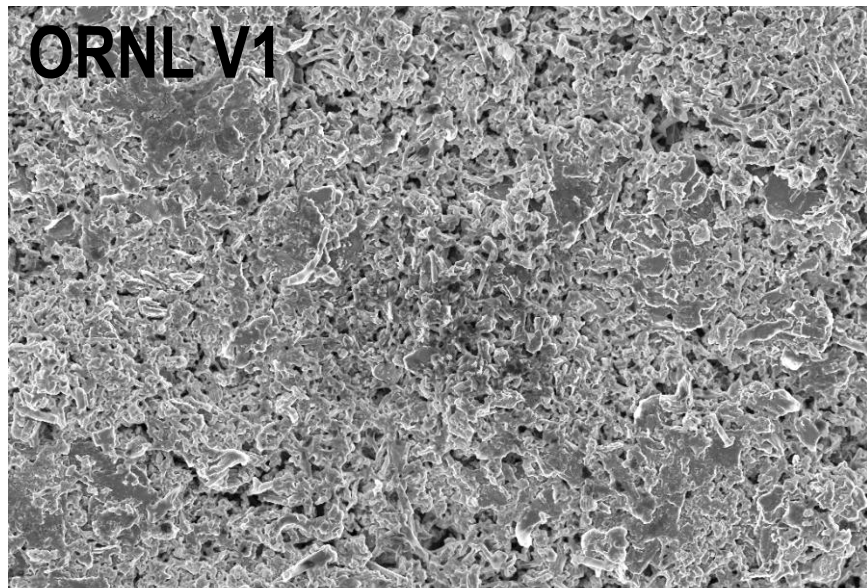


*calculated from 50 Ah cell scale up

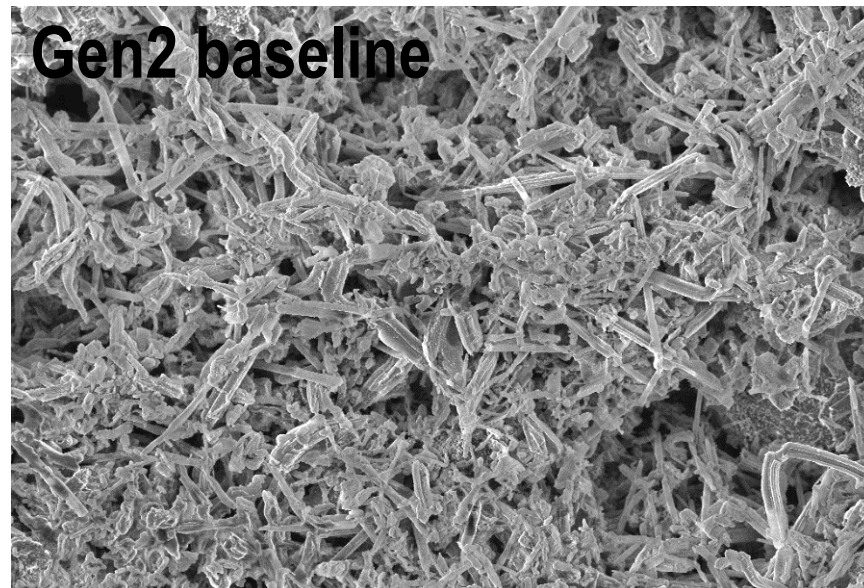


Uniform Li plating with graphite layer clearly seen underneath.

Difference in Li plating morphologies when different electrolytes were used

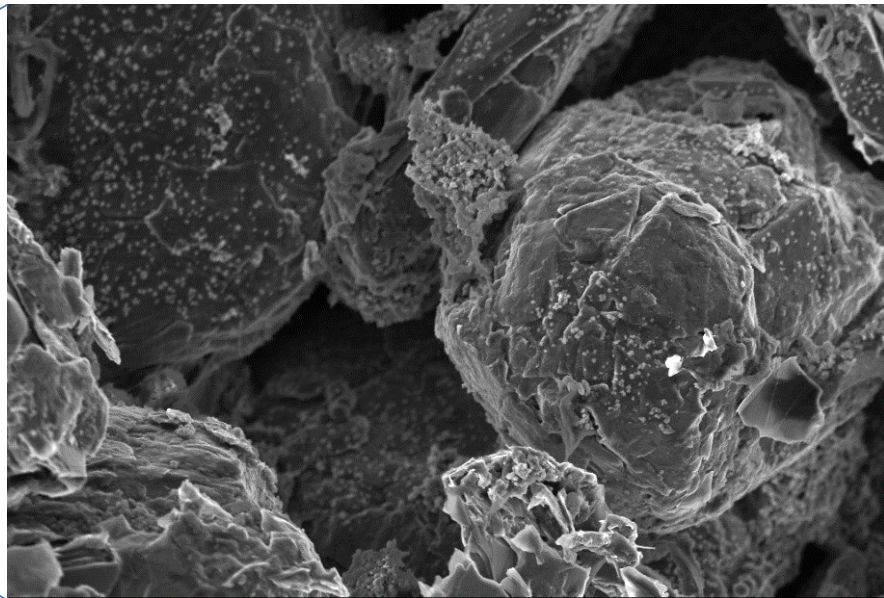
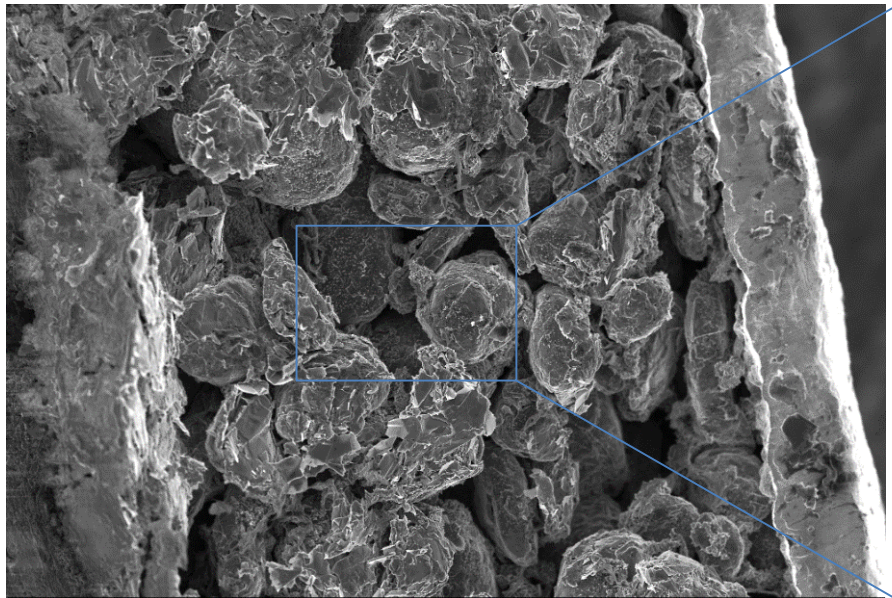


5 μ m



Dendritic Li plating in Gen2 electrolyte

Li plating is mainly at the separator / graphite interface



10 μm

2 μm

Li deposits

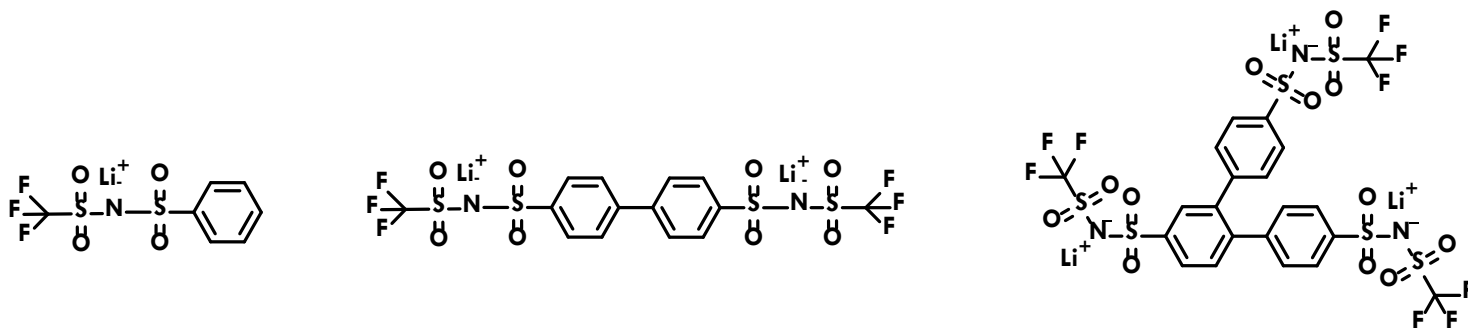
Synthesize well-defined oligomer-type Li salt for further improvement in t_{Li+}

Transference Number

$$t_+ = \frac{\mu_+}{\mu_+ + \mu_-}$$

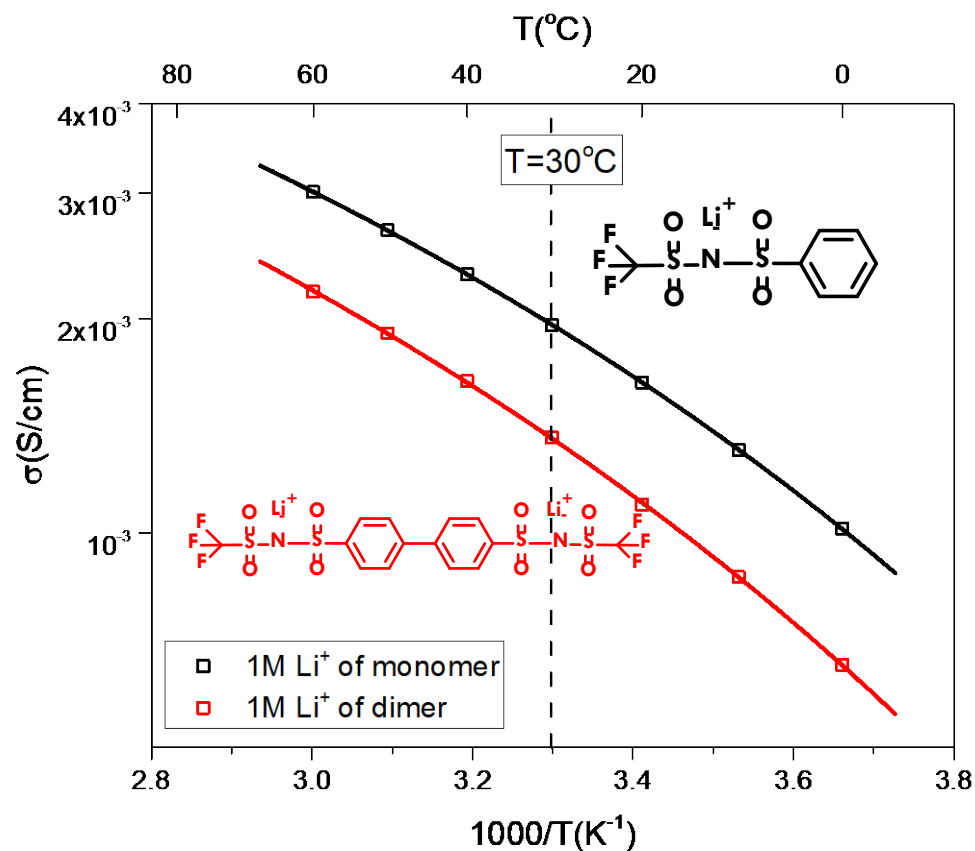
Lithium ion mobility can be increased *via* slowing the counteranion mobility, leading to higher transference numbers and better faster-charging performance

Well-defined Li salt with high transport number for fast charging project



Synthesis and test of well-defined oligomer with one, two or three Li on one molecule: transport number effect on fast charging.

Li salt in dimer format lowers the ionic conductivity compared to monomer



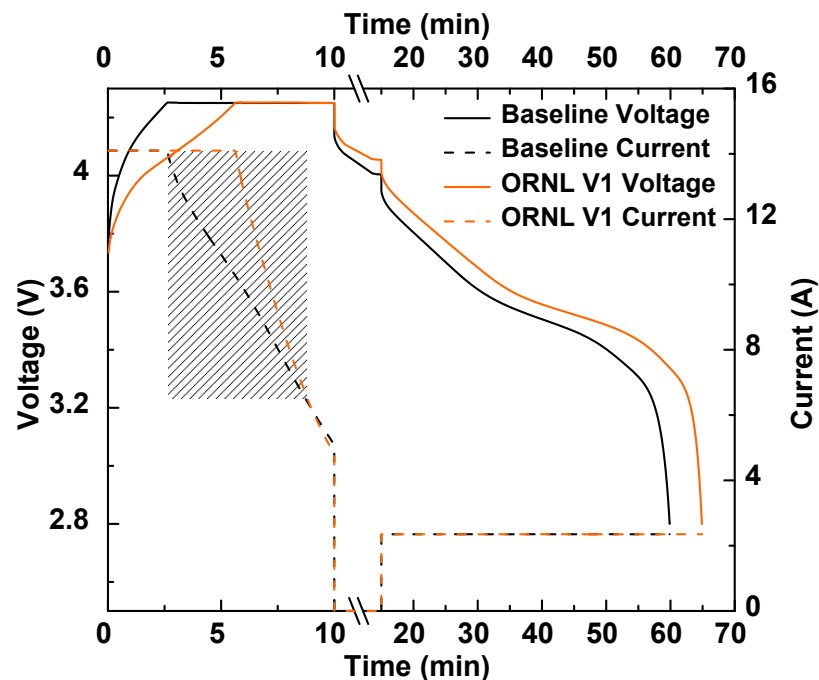
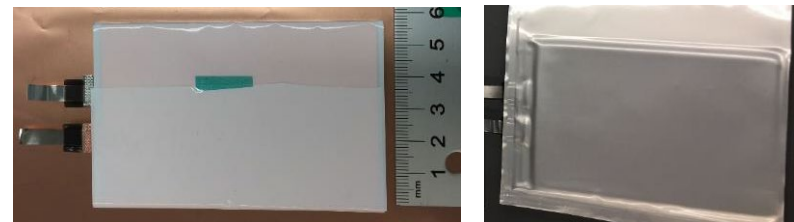
Solvent: EC/EMC=3:7 (weight ratio)
Concentration: 1mol/L of Li^+

$\sigma_{30^{\circ}C}(\text{monomer}) = 1.96 \text{ mS/cm}$

$\sigma_{30^{\circ}C}(\text{dimer}) = 1.36 \text{ mS/cm}$

ORNL V1 vs Baseline in 2.33 Ah pouch cell shows ~13% improvement

2.33 Ah pouch cells at 201 Wh/Kg level.
Scale up to 50 Ah cell at 222 Wh/Kg level.



Energy density XFC Wh/Kg	In 2.33 Ah cell	Scale up to 50 Ah cell
ORNL V1 cell	161	178
Baseline cell	143	158

- ORNL V1 cell shows 5.59 minutes CC charge compared to 2.59 minutes CC charge of baseline cell.
- ORNL V1 cell has 1.954 Ah capacity retained, compared to 1.757 Ah capacity retained.

This 13% energy density improvement has been confirmed by third-party testing

Selected Responses to Specific FY19 DOE AMR Reviewer Comments

- It should be ensured that the new co-solvent does not impact the high temperature calendar life or make the safety characteristics worse compared to the baseline systems.
- ✓ *Fast charging was demonstrated to increase cell temperature to a higher degree (J Electrochem Soc 166 (2019) A3254). Therefore, the co-solvents in this study should have the high temperature feature in the calendar life testing.*
- The reviewer pointed out that regarding the anion oligomers, the gain in the transference number may be overshadowed by the reduction in conductivity.
- ✓ *This is a plausible argument. We do see a reduction in conductivity when an anion oligomer is used. Therefore, the team has been spending more efforts on LiFSI formulation.*
- Also, the aluminum passivation characteristics of the new salt may not be as efficient as with LiPF₆ and need to be verified.
- ✓ *This year we have conducted the CV test of our electrolyte towards Al foil. With adequate additive in the formulation, no corrosion of Al foil was found.*
- The project may explore atomistic/MD simulations to understand the mechanisms that should in turn help seek alternative hybrid electrolytes.
- ✓ *We welcome future collaboration to help the understanding how electrolyte can be designed and developed for fast charging.*

Proposed Future Research

- Further evaluation of more electrolyte additives on 10-minute fast charging vs. baseline electrolyte.
- Test new Li oligomer salts for fast charging performance in Li-ion cells.
- Increase electrode areal loading and test performance incorporating the new electrolyte.
- Post-mortem test of Li-ion cells after finishing fast charging cycles.
- Deliverables for final project 2 Ah cells.

Any proposed future work is subject to change based on funding levels.

Summary

- **Objective:** To implement a novel high-Li-ion-transference (Hi-LiT) electrolyte and enable a 10-minute charge of cells with 180 Wh/kg energy density by increasing t_{Li^+} from 0.36 to 0.75 while maintaining a relatively high conductivity of 4-10 mS/cm.
- **Approach:** (1) Innovative Li salt anion oligomers to suppress anion mobility and increase Li ion transference number. (2) Formulations with multiple solvent systems to provide better Li ion mobility and suppress Li plating. (3) Anion receptor additives to further immobilize anions and dissociate cations in electrolyte.
- **Technical:** Successfully studied LiFSI as the salt in electrolyte formulation for fast charging. The additives used in the formulation prevent aluminum corrosion. ORNL electrolyte formulation shows 13% energy density improvement compared to baseline Gen2 electrolyte in initial 10-minute fast charging, and 35% capacity retention after 600 cycles.
- **Collaborators:** David Robertson, ANL; Guangsheng Zhang, UAH; Feng Lin, Virginia Tech; Michael Schulz, Virginia Tech; Kejie Zhao, Purdue; Jue Liu, SNS ORNL.

Acknowledgements



- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (Technology Manager: Brian Cunningham)



- Team members:
 - Zhijia Du
 - David Wood
 - Tomonori Saito
 - Alexei Sokolov
 - Kris Inman (XALT)
 - Pengfei Cao
 - Xianyang Wu
- Technical Collaborators
 - David Robertson, ANL
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 - Jue Liu, SNS

Information Dissemination

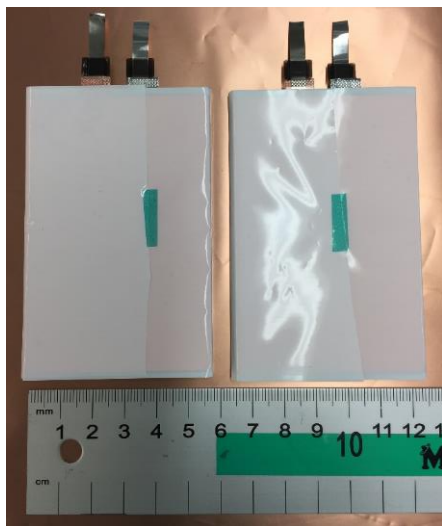
Journal Papers and Presentations

- Z. Du, D. L. Wood, I. Belharouak, Enabling fast charging of high energy density Li-ion cells with high lithium ion transport electrolytes, *Electrochemistry Communications* 103 (2019): 109-113.
- Shan Huang, Xianyang Wu, Gabriel M. Cavalheiro, Xiaoniu Du, Bangzhi Liu, Zhijia Du, Guangsheng Zhang, In Situ Measurement of Lithium-Ion Cell Internal Temperatures during Extreme Fast Charging, *J Electrochem Soc* 166 (14), A3254-A3259.
- Tianyi Liu, Zhijia Du, Xianyang Wu, Muhammad M. Rahman, Dennis Nordlund, Kejie Zhao, Michael D. Schulz, Feng Lin, David L. Wood, III, Ilias Belharouak, Effect of fast charging on the electrodes in Li-ion cells, submitted.
- Xianyang Wu, Tianyi Liu, Yaocai Bai, Feng Xu, Muhammad Rahman, Cheng-Jun Sun, Feng Lin, Kejie Zhao, Zhijia Du, Effects of Solvent Formulations in Electrolytes on Fast Charging of Li-ion Cells, submitted.

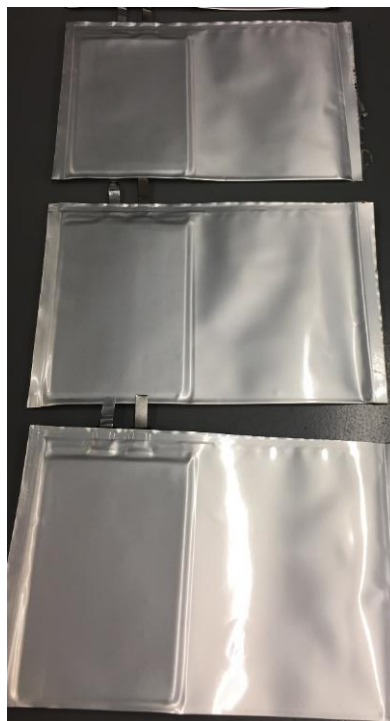
Thank you for your attention!

Deliverable 1

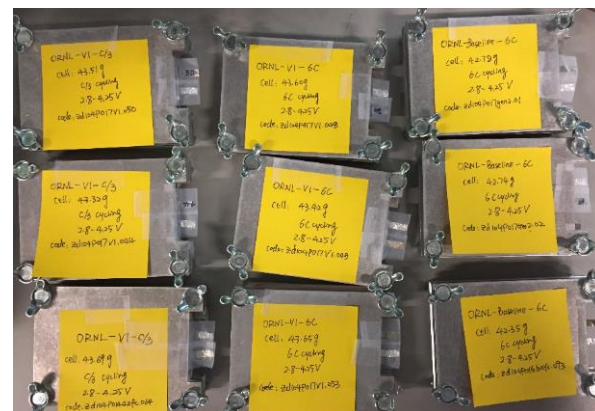
2.33 Ah pouch cells at 201 Wh/Kg level.
Scale up to 50 Ah cell at 222 Wh/Kg level.



Jelly roll of the
2.33 Ah pouch cell.



Vacuum sealed
pouch cells



Pressure clamped pouch
cells

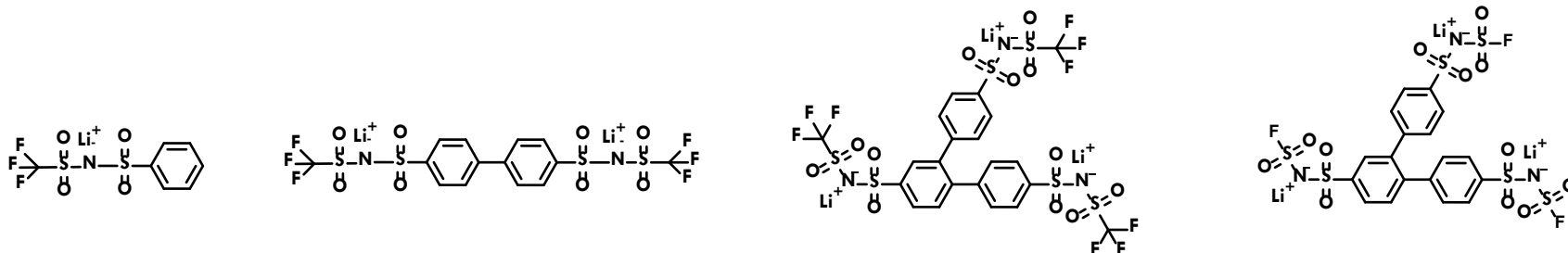
Synthesize well-defined oligomer-typed Li salt for further improvement in t_{Li^+}

Transference Number

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Lithium ion mobility can be increased *via* slowing the counteranion mobility, leading to higher transference numbers and better faster-charging performance

Well-defined Li salt with high transport number for fast charging project



Synthesis and test of well-defined oligomer with one, two or three Li on one molecule: transport number effect on fast charging

After initial battery testing of Li^+TFSI^- oligomers, the Li^+FSI^- oligomer will be synthesized: effect of TF and F